

Reactively sputtered RuO₂ diffusion barriers

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The thermal stability of reactively sputtered RuO₂ films is investigated from the point of view of their application as diffusion barriers in silicon contact metallizations with an Al overlayer. Backscattering spectra of Si/RuO₂/Al samples and electrical measurements on shallow junction diodes with (Si)/TiSi_{2,3}/RuO₂/Al contacts both show that RuO₂ films are effective diffusion barriers between Al and Si for 30-min annealing at temperatures as high as 600 °C.

Diffusion barriers are widely used in contact metallization schemes to preserve the integrity of shallow junctions during post-metallization processing. Refractory metal nitrides (e.g., TiN, W-N)¹⁻⁴ have emerged as a leading class of materials for diffusion barrier purposes. These transition metal nitrides have attracted much interest because of their low resistivity and stability at high temperatures when in contact with a metal overlayer (e.g., Al, Au, Ag). In contrast, very little is known about the applicability of conducting transition metal oxides as diffusion barriers. One reason for the scarcity of information is probably the fact that the most stable transition metal oxides are electrically insulating. Recently, RuO₂ films deposited by metalorganic chemical vapor deposition have been investigated so far for diffusion barrier applications.⁵ In this letter, we report on reactively sputtered RuO₂ films and demonstrate that they are superior to TiN as diffusion barriers between Al and Si.

Substrates of (111) oriented *n*-type Si with 0.005 Ω cm resistivity were used throughout the experiment to study the metallurgical interactions of the (Si)/RuO₂/Al system. The *n*⁺*p* shallow junctions for testing the performance of (Si)/TiSi_{2,3}/RuO₂/Al contacts were prepared on (100) oriented *p*-type Si with 10–20 Ω cm resistivity. After an initial growth of wet oxide of 4500 Å, three photolithographic steps were followed to fabricate the junctions and metallizations. The first mask defined the diffusion areas of 500 × 500 μm². The junctions were formed by implantation at room temperature of 7 × 10¹⁵ As/cm² of 150 keV into the diffusion openings through a 600-Å-thick screen oxide formed previously by dry oxidation. Dopant activation and drive-in were accomplished subsequently by annealing the wafers at 1000 °C for 30 min in an N₂ ambient. The second mask was then applied to open contact windows of 300 × 300 μm² in the thin oxide with a buffered HF solution. Finally, a third mask was used to define the metallization area. The (Si)/TiSi_{2,3}/RuO₂/Al contact pattern was then delineated by the lift-off technique. The completed diodes have junction depths of ~0.35 μm and As surface concentrations of about 3 × 10²⁰ cm⁻³, as indicated by the SUPREM simulation program.

The deposition of films was performed in an rf sputtering system equipped with a diffusion pump and a cryogenic baffle. Magnetron-type circular cathodes (7 cm diameter) were used as the sputtering source. Prior to loading into the sputtering system, the Si wafers were first slightly oxidized in an oxygen plasma and then etched in 1:10 HF:H₂O solu-

tion. The sputtering chamber was evacuated to a base pressure of about 1 × 10⁻⁶ Torr before deposition. To sputter the titanium silicide films, a composite TiSi₂ target and pure argon were used. The films had a nominal composition of TiSi_{2,3}, as determined by backscattering spectrometry, and were 300 Å thick. RuO₂ films were reactively sputtered in 10 mTorr of a 50% O₂ and 50% Ne mixture with 500 W sputtering power. The thickness of the films was 400 Å. Aluminum overlayers (2800 Å for the Si/RuO₂/Al metallization samples, and 5000 Å for diodes) were sputter deposited in argon. All metal films were deposited without breaking the vacuum in the sputtering system. The samples were then annealed in a vacuum furnace at a pressure below 5 × 10⁻⁷ Torr in the range of 500–650 °C for 30 min. The thermal stability of contacts was analyzed by backscattering spectrometry and electrical measurements.

The RuO₂ films tested in this study were single phase as indicated by x-ray diffraction with Read camera with resistivity of about 120 μΩ cm. The spectra of Fig. 1 show that within the resolution of backscattering spectrometry, there is no change in a Si/RuO₂/Al sample before and after annealing at 650 °C for 30 min. The electrical characteristics of a shallow *n*⁺*p* junction with the (Si)/TiSi_{2,3}/RuO₂/Al contact scheme are presented in Fig. 2. The dc characteristics of the diodes prior to any heat treatment show a reverse leakage current density of about 3 × 10⁻⁸ A cm⁻².

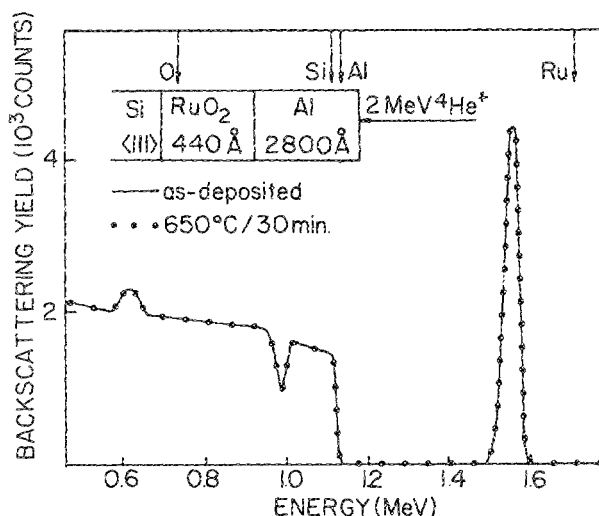


FIG. 1. Backscattering spectra of Si/RuO₂/Al sample before and after annealing at 650 °C for 30 min.

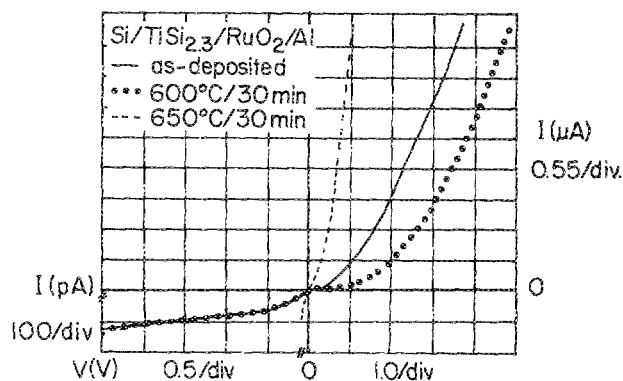


FIG. 2. Electrical characteristics of diodes with the Si/TiSi_{2.3}/RuO₂/Al metallization before and after annealing at 600 and 650 °C for 30 min.

After annealing at 600 °C for 30 min, the leakage current remains constant but the forward voltage drop rises slightly. The diodes subjected to heat treatment at 650 °C for 30 min were all shorted. However, backscattering spectra do not show any signs of reactions between the layers at this temperature. Scanning electron microscopy was used to elucidate the failure mechanism of the diodes. To see the RuO₂ surface, the Al overlayer was selectively etched in a HCl/HNO₃ solution. The as-deposited sample exhibits very smooth surface morphology. For samples annealed at 650 °C for 30 min, the presence of localized pits and fractures was observed on the RuO₂ surface. Diode failures can be connected with diffusion of Al through these weak spots. Interdiffusion through these spots is probably too small to be detected by backscattering spectrometry.

Electrical measurements on *pn* shallow junction diodes with Si/TiSi₂/Al contacts reported previously⁶ showed that the device junctions were all shorted after annealing for 30

min at 400 °C. This indicates that the presence of a RuO₂ diffusion barrier enhances dramatically the thermal stability of the Si/TiSi₂/Al contact. It is also interesting to note that even such a thin film of RuO₂ like 400 Å is able to act as a good diffusion barrier. For comparison, previous reports (such as those by Ting and Wittmer¹ and Nygren *et al.*⁷) showed that the shallow junctions with Si/Ti(TiSi₂)/TiN/Al are not stable after annealing at 400–550 °C for 30 min (increasing leakage) and at 475 °C for 30 min, respectively.

This study shows that sputtered RuO₂ has very interesting properties in terms of application of this material as diffusion barriers in very large scale integration technology.

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¹C. Y. Ting and M. Wittmer, *Thin Solid Films* **96**, 327 (1983).

²S. Kanamori, *Thin Solid Films* **136**, 195 (1985).

³H. P. Kattelus, E. Kolawa, K. Affolter, and M-A. Nicolet, *J. Vac. Sci. Technol. A* **3**, 2246 (1985).

⁴H. P. Kattelus and M-A. Nicolet, in *Diffusion Phenomena in Thin Films*, edited by D. Gupta and P. S. Ho (Noyes, New Jersey, in press).

⁵M. L. Green, M. E. Gross, L. E. Papa, K. J. Schnoes, and D. Brasen, *J. Electrochem. Soc.* **132**, 2077 (1985).

⁶C. Y. Ting and M. Wittmer, *J. Appl. Phys.* **54**, 937 (1983).

⁷S. Nygren, R. Buchta, V. Sustafsson, H. Norström, P. Wiklund, M. Östling, and C. S. Petersson, in *Proceedings of 11th Nordic Semiconductor Meeting* (Espoo, Finland, 1984), p. 271.